River carries very low suspended particulate matter to its estuary compared to other major rivers. As a result, low concentrations of particulate organic carbon (POC) are observed downstream in opposition to relatively high concentrations of dissolved organic carbon (DOC). We investigate sources, cycling and fluxes of both dissolved and particulate organic carbon in the St. Lawrence River from its source (the Great Lakes outlet) to its estuary, as well as in two of its tributaries. Special attention is given to seasonal patterns by using data collected on a bi-monthly basis from mid-1997 to late 2001. Concentrations and δ^{13}C measurements of dissolved inorganic carbon (DIC), DOC and POC as well as elemental dissolved organic matter (DOM) and particulate organic matter (POM) C:N ratios are used to calculate carbon fluxes and to discriminate aquatic vs. terrigenous sources. In the St. Lawrence River itself, POC is mainly of aquatic origin and is depleted in ^{13}C by roughly 13$^{o}/_{oo}$ vs. dissolved CO_2. In the Ottawa River, St. Lawrence River's most important tributary, POM seems to be mainly terrigenous. In a small tributary of the St. Lawrence River, POM is aquatic in summer and terrigenous in winter. DOM seems to be terrigenous at all sampling sites with some influence of DOM derived from aquatically produced POC in summer in the St. Lawrence River at the outlet of the Great Lakes as well as one of its small tributaries. Flux calculations suggest that DOC is heavily degraded in the riverine portion of the St. Lawrence system in summer and fall. On a yearly basis, DOC losses represent about 10% of DOC exports to the estuary. The St. Lawrence River annually exports 1.38 x 10^{12} g of DOC (2000-2001), 0.11 x 10^{12} g of POC (average for 1999 and 2000) and 5.4 x 10^{12} g of DIC into its estuary. Finally, carbon fluxes from the St. Lawrence River to its estuary can be estimated from water discharge rates.

H12A-04 1115h

Constraining the Variability in Ages, Sources and Reactivity of Organic Matter Transported by Rivers of the Northeast U.S. to the Ocean Margin

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Riverine transport of organic carbon (OC) is a significant flux in the global C budget, representing major terms for both terrestrial losses and ocean margin inputs. Rivers are also dynamic systems where the chemical and isotopic character and reactivity of terrestrial OC is modified prior to its export to the margins. However, several major unknowns still exist in land-ocean OC fluxes, including: i) the amounts, ages and character of the OC reservoirs mobilized and transported; ii) the scales of variability in these parameters both within and among different systems; iii) the extent of modification of these parameters by microbial and abiotic processes during riverine and estuarine transport. The use of natural radiocarbon in aquatic and marine studies provides unique source, turnover and processing information with respect to local, regional and global carbon budgets. However, the number of C-14 analyses in most river systems is often too small, thus limiting the full potential of this isotope in carbon studies. As part of our on-going work, we are measuring the C-14 signatures and ages of dissolved and particulate organic carbon (DOC and POC, respectively), as well as dissolved inorganic carbon (DIC), in a group of northeast U.S. rivers. Here we report the ranges in radiocarbon signatures of bulk DOC, and POC, DIC and their associated 13C/12C ratios from measurements on seven different river systems. The rivers studied occupy a relatively small geographic range, yet individually they export both ancient and fully modern average-aged C to the coastal ocean. In addition, microbial heterotrophy appears to be responsible for the loss of both contemporary and highly aged OC, depending upon the dominant sources to a given system. While sample numbers still preclude an in-depth understanding of the sources and fates of different aged components in river systems in general, the data set permits some preliminary conclusions concerning the relative importance of wetlands, ancient marine organic matter, and within- system modification as key potential controls on riverine C ages.

H12A-05 1130h

Results From A High Resolution In-Situ Water Quality Monitoring Program: What We Don't Know About Nitrate Flux from Watersheds

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Measuring the flux of nutrients from watersheds to the coastal ocean is important because increasing nitrogen, phosphorus and sediment loads in may rivers are degrading aquatic ecosystems. Management programs aimed at reducing nitrate contamination in surface waters need a comprehensive understanding of sources and fundamental processes that control water quality on a watershed scale. Over the past three years, the RiverNet Monitoring Program has made hourly measurements of nitrate concentrations at six stations in the Neuse River Basin, NC on the mid Atlantic coastal plain. Hourly nitrate concentrations exhibit significant variations on short (hourly to daily) time scales associated with point source dischargers. Nitrate fluxes calculated from hourly measurements differ from daily-calculated fluxes by 10% to 30% depending upon discharge conditions. These findings indicate that significant errors can be produced by monitoring programs that try to determine long-term trends of basin scale nitrogen flux without high-resolution data sets in basins with large point sources. Isotope techniques have been used to identify nitrogen sources and describe nitrogen transformations in watersheds and groundwater. Nitrogen, oxygen, and carbon isotopes of nitrate and POM indicate that in-stream nutrient consumption in the main channels is not an important process in nitrate transport to the estuary. This system is light limited by sediment turbidity, yet the concentration of nitrate deceases down basin. Geology and groundwater hydrology influence nutrient/discharge relationships. Dissolved phosphate and HD / ^{18}O values of river and groundwater indicate that decreased nitrate concentrations in the lower basin result from significant deep groundwater addition and not in-stream consumption. In urban and agricultural watersheds, ^{15}N / ^{18}O relationship of nitrate indicates that atmospheric deposition may be important. ^{17}O measurements of riverine and groundwater nitrate indicate that atmospheric deposition can be a significant contributor (90%) to nitrate flux in urban watersheds, but contributes less than 10% of the nitrate flux in the basin as a whole. In the Neuse River basin, water discharge and nitrogen flux are positively correlated to ENSO variations (El Nino Southern Oscillation Index). Long-term nitrogen flux trends must take the ENSO cycle into account. These results indicate that current monitoring programs have tremendously underestimated the flux of nitrogen to the coastal ocean.

URL: http://rivernet.ncsu.edu

H12A-06 1145h INVITED

Hydrologic and Biogeochemical Controls on the C and N Isotopic Compositions of Particulate Organic Matter in Large US Rivers

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Particulate organic matter (POM) samples were collected bi-weekly to monthly from 40 NASQAN (National Stream Quality Accounting Network) river sites in the Mississippi, Colorado, Rio Grande, and Columbia River Basins from 1996 to 2001. These samples were analyzed for carbon and nitrogen stable isotopic compositions, and C:N ratios. The goal of our study was to use the isotopic compositions of POM samples, along with the abundant ancillary chemical and hydrological data generated by the NASQAN program at the same sites and dates (http://water.usgs.gov/nasqan/), to quantify seasonal and spatial changes in the POM and other nutrient sources, and to investigate in-stream biogeochemical processes in these large river systems. The d13C values for these sites ranges from less than -40 to about -17 permil. The d15N values range from about -30 to +30 permil. The combined use of the isotope data, C:N values, water chemistry, and hydrological data allow the determination of the seasonal changes in the contributions of POM from different terrestrial and riverine sources. These data also provide insight into seasonal and spatial controls on sources of nutrients to the rivers and biogeochemical processes in the water column. On average, about half of the POM from these rivers is composed of plankton and/or heterotrophic bacteria. However, there is considerable seasonal variation in the relative proportions, mainly related to algal blooms and seasonal changes in discharge amounts from different upstream sources. Our data suggest POM derived from in-stream productivity, since it is biologically labile, may be an important but overlooked contributor to hypoxia in the Gulf of Mexico and other coastal areas.

H12B CC: 520 A Monday 1030h

Remote Sensing, Hydrology, and Field Experiments II

Presiding: **T J Jackson,** USDA Agricultural Research Service**; B Crosson,** Global Hydrology and Climate Center

H12B-01 1030h

Reanalysis Approach to Land Data Assimilation

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A reanalysis data assimilation framework in which remote sensing measurements are merged with a conventional land surface model to estimate soil moisture (surface and profile) and associated surface fluxes is presented. Formally known as smoothing in the control literature, the framework combines data from future and past an estimation time to form an estimate. This is differs distinctly from filtering which uses data sequentially, yielding an estimate based only on current and past data. Through use of additional information on how the system evolves, the smoothing approach yields improved estimates of the state at the present time. Traditional smoothers such as the Rauch-Tung-Striebel (RTS) smoothers are optimal batch estimators as Kalman filters are optimal sequential estimators. Nevertheless in their traditional form both are limited to linear systems. Linearization of either the Kalman filter or the RTS smoother is seriously prone to unstable growth of the covariance matrices. Artificial limits on the propagation of the covariance matrix can result in suboptimal filters and poor estimation. Ensemble techniques have been developed for Kalman filters in order to avoid the linearization of the system equation. The framework presented here builds an ensemble smoother from a successful ensemble Kalman filter. An advantage of ensemble techniques is that we do not need to linearize or find the adjoint of the model, so we can use a mainstream land surface model (such as the NOAH Land Surface Model) in the data assimilation framework. By using a reanalysis rather than filtering approach, we can extract more information from the observational data available. The development and testing of the ensemble smoother as well as its application to land data assimilation is presented.

H12B-02 1045h

Variational Assimilation of Multi-Sensor Satellite Imagery for the Estimation of Evaporation from Soil and Vegetation

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Turbulent fluxes from the surface do not have a unique signature that can be detected by remotely deployed instruments. In order to retrieve the land evaporation, the remotely sensed measurements ned to be merged into models that infer fluxes from their covariations. This study is based on variational assimilation of Land Surface Temperature (LST) into a surface energy balance model. It does not require empirical relations such as those relating evaporation to vegetation indices and LST nor does it require closure assumptions such as those that assume ground heat flux is a given fraction of peak net radiation. This study recognizes that there are two major unknown parameters in the estimation of land evaporation (near-surface air turbulent conductivity and evaporative fraction). Uncertainties about the values for these parameters drive the errors of estimation. This study advances the approach in two major new directions. First and foremost it re-casts the variational assimilation system as a multi-scale framework where satellite LST estimates from several sensors are assimilated. Secondly the remotely sensed LST treated as a combination of contributions from the canopy and the bare soil surface. Application of the assimilation system to a large area within the U.S. Great Plains is shown. Spatial patterns of the retrieved parameters and their correspondence to observed land use maps and their consistency with seasonal phenology across the Great Plains are demonstrated. The daytime total latent heat flux maps (across the Great Plains domain) for the several periods within the Summer of 1997 and resulting from the assimilation system are presented. These maps represent the ultimate goal of the approach.

H12B-03 1100h

Retrieving Soil Moisture States Using Streamflow Assimilation

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It has been shown that soil moisture has an important impact on seasonal to interannual climate prediction through evapotranspiration controls, especially in heavily forested areas like the Amazon. Hence, it is important that the land surface component of climate models have an accurate initialisation of soil moisture. While remote sensing of soil moisture holds much promise for near-surface soil moisture measurement, and root zone soil moisture retrieval when assimilated into a land surface model, its application to such heavily forested areas is limited. This is due to the masking effect of dense vegetation canopies on remote sensing signals. However, soil moisture also has a strong impact on streamflow, through its control on baseflow and partitioning of rainfall into infiltration and runoff. Thus the use of streamflow data to constrain model predicted soil moisture is a potentially viable alternative to near-surface soil moisture remote sensing. This research demonstrates this potential using a synthetic twin-experiment. The study is based on typical conditions for both a semiarid and humid environment, using the catchment-based land surface model used by NSIPP (NASA Seasonal to Interannual Climate Prediction Project). First we produce a "truth" dataset which provides the streamflow observations and soil moisture validation data. Second, we make an "openloop" simulation where only the initial soil moisture states have been degraded to represent our lack of knowledge on soil moisture. We then assimilate streamflow observations from the truth run into the degraded simulation, in order to retrieve back the true initial soil moisture states. The results shown from this demonstration are for single subcatchments of much larger catchments, so that runoff routing could be ignored. Future research will include larger nested catchments interconnected via a routing model.

H12B-04 1115h

Testing Remotely Sensed Evapotranspiration Estimates Using Airborne and Ground Measurements

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Evapotranspiration (ET) is a key hydrologic flux that is rarely monitored. Remotely sensed measurements of land surface characteristics, including surface temperature, in combination with surface energy balance models provide an opportunity to improve the frequency and accuracy of ET estimates. Here we compare results from two ET estimation models with ground and airborne measurements of latent and sensible heat fluxes from an irrigation district in South-Eastern Australia during January 2003 (mid-summer). The irrigation district contains a mixture of wet and dry patches at the scale of hundreds of metres. Ground data collected during the field campaign include eddy covariance measurements of latent and sensible heat flux at two sites, a variety of associated meteorological measurements and detailed soil moisture and vegetation (NDVI) patterns about these sites. The airborne data include eddy covariance measurements of latent and sensible heat flux, line measurements of surface temperature, and detailed (1m resolution) NDVI images over the field sites. Landsat ETM+ and ASTER images are available during the field campaign. ET estimates from these images are made with a two-source model and the Surface Energy Balance Algorithm for Land (SEBAL). Results of comparisons of these with the ground and airborne data will be presented and the models will be intercompared. Some issues with the spatial averaging techniques for the airborne flux data will be discussed.

H12B-05 1130h

Large-Scale Soil Moisture Observations Using the Advanced Microwave Scanning Radiometer During the 2002 Soil Moisture Experiment

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Soil moisture is of fundamental importance to many hydrological, biological and biogeochemical processes. Improved characterization of surface soil moisture can lead to significant forecast improvements of weather patterns and precipitation. However, the heterogeneous nature of soil moisture creates difficulty in obtaining in situ large-scale regional values needed for numerical weather models simulations. Microwave remote sensing allows frequent, regional and global-scale soil moisture patterns to be observed with confidence. The launch of NASA 's Aqua satellite on 4 May, 2002 provided the first opportunity for high temporal, global-wide soil moisture to be observed. The Advanced Microwave Scanning Radiometer for the Earth Observing System (AMSR-E) instrument onboard Aqua improves the spatial resolution and frequency range of earlier generations of passive microwave instruments. In this study, 10.69 GHz and 6.9 GHz brightness temperatures are simulated using collected in-situ ground data in an attempt to analyze heterogeneity effects and moisture retrieval methods for comparison with available observed AMSR-E and the airborne C-band Polarimetric Scanning Radiometer (PSR/C) data during the 2002 Soil Moisture Experiment (SMEX02) in Iowa. A description of the model simulation and heterogeneity effects is given in addition to comparisons of simulated and observed brightness temperatures of both instruments. These studies will help us to gain confidence in using the AMSR derived soil moisture in regions of the world which lack in situ observations.

H12B-06 1145h

Effects of land-use modification on surface fluxes and climate: A numerical mesoscale study over Southeastern Turkey

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Over the course of last two decades, Southeastern Turkey has experienced major land-use changes, primarily in the form of irrigated agriculture. Recent work by authors based on remote sensing and observational climatology indicate that irrigation has significantly altered the hydrologic fluxes mainly through changes in wind velocities. To further understand the mechanisms by which hydrologic fluxes are affected as well as to assess potential climatic impacts of irrigation, we used a fine-scale (10 km) nested regional model. Two different simulations were conducted. The first experiment has a small domain, designed to capture the effects of progressive irrigation on hydrologic fluxes under different initial surface conditions. The second experiment has a larger domain with the main goal of determining climatic influences of irrigation under current and future irrigation scenarios. The results from the first experiment show that irrigation significantly affects the partitioning of water between the land surface and the atmosphere during summer months. The area-averaged model results for the second experiment indicate significant differences in humidity, temperature, and wind direction between the control (no irrigation) and irrigated runs under present and future land-use scenarios. Overall, these experimental results suggest that land-use modifications involving irrigation has strongly modified the lower atmosphere over Southeastern Turkey in a way that appears consistent with Bouchet's complementary theory.

H12C CC: 520 F Monday 1030h

Understanding Flow and Reactive Transport Processes in Sulfide-Bearing Porous Material II

Presiding: **J W Molson,** Ecole Polytechnique**; R Lefebvre,** Institut National de la Recherche Scientifique

H12C-01 1030h INVITED

Recent Advances in Numerical Modeling of Reactive Chemical Transport in Sulfur-Bearing Rock-Fluid Systems

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Redox processes that involve sulfur-bearing mineral phases play a crucial role in the development of ore deposits, in the degradation of mining wastes, and in geologic disposal and sequestration of sour gases. The underlying processes involve considerable physical and chemical complexity, and microbial interactions may play an important role as well. Fluid flow and mass transport typically take place in settings that involve heterogeneities on multiple scales, and may be dominated by fast preferential pathways such as fractures. Both aqueous and gas phases may actively participate in chemical interactions, and redox processes that are kinetically controlled may play a dominant role. System behavior is further complicated by non-stoichiometric and metastable mineral phases, and by feedbacks between hydraulic, chemical, and thermal effects. Effective processes and their characteristic parameters are dependent on space and time scales, and vastly different time scales can be relevant for the hydraulic and chemical systems. The complexity and diversity of sulfur-bearing rock-fluid systems is illustrated with two examples of reactive transport, the supergene enrichment of copper protores due to weathering processes during desertification over geologic time, and the disposal of gas mixtures including SO_2 and H_2S through underground injection. We highlight the description of physical and chemical processes, mathematical modeling approaches, numerical solution techniques, and illustrative results. Mineral assemblages in natural analog systems provide important constraints for thermodynamic data, that must be honored in order that realistic results may be obtained. Our paper concludes with a summary of current challenges for modeling reactive chemical transport. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

H12C-02 1045h

Prediction and Control of Air Flow in Acid-Generating Waste Rock Dumps

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